Photon-Echo Relaxation Measurements with Two Dye-Lasers. Application to Pentacene-h14 and -d14 in p-Terphenyl-h14 Crystals at 1.5 K

Morsink, Jos B.W.; Aartsma, Thijs J.; Wiersma, Douwe A.

Published in:
Chemical Physics Letters

DOI:
10.1016/0009-2614(77)80436-3

Publication date:
1977

PHOTON-ECHO RELAXATION MEASUREMENTS WITH TWO DYE-LASERS. APPLICATION TO PENTACENE-h_{14} AND -d_{14} IN p-TERPHENYL-h_{14} CRYSTALS AT 1.5 K

Jos B.W. MORSINK, Thijs J. AARTSMA and Douwe A. WIERSMA
Laboratory for Physical Chemistry, Univeristy of Groningen, Groningen, The Netherlands

Received 13 April 1977

Electronically controlled photon-echo relaxation measurements, using two nitrogen pumped dye-lasers, are reported for mixed crystals of pentacene-h_{14} and -d_{14} in p-terphenyl-h_{14} at 1.5 K. In dilute mixed crystals (ca. 10^{-8} M) the photon-echo lifetime is found to be exclusively determined by the fluorescence lifetime. *Homogeneous linewidths* of 7.1 and 5.9 MHz at 1.5 K are then calculated for the electronic origin of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of pentacene-h_{14} and -d_{14} respectively. The decrease in photon-echo lifetime at higher guest concentrations (ca. 10^{-7} M) is ascribed to *energy transfer* between excited and neutral guest molecules.

1. Introduction

Photon-echo relaxation measurements sofar, have been a tedious and time-consuming business [1–3]. The main problem is the control over the delay between the first exciting and the second probe pulse. Quite often an optical delay line [1] is used to generate, in discrete steps, the probe-pulse delay. The extreme sensitivity of the echo-intensity towards the spatial overlap of the laser beams make such a relaxation measurement a nontrivial matter. Patel and Slusher [4] largely solved this problem by using two separate CO_2 lasers for the exciting and probe pulse. Unfortunately they still had only *mechanical* control over the pulse separation. In this letter we show that reliable photon-echo relaxation measurements can be made by using two independently triggered nitrogen-pumped dye-lasers for the exciting and probe-pulse. The pulse separation in this case is *electronically* controlled and the measurements can therefore be completely automated.

Photon-echo decay-time measurements, performed with this system, are reported for the mixed crystals of pentacene(PTC)-h_{14} and -d_{14} in p-terphenyl-h_{14} at 1.5 K. In dilute mixed crystals (ca. 10^{-8} M) the coherence lifetime (T_2) is found to be only determined by the fluorescent decay of the upper state. At higher concentrations (ca. 10^{-7} M) T_2 considerably shortens, which implies that energy transfer (spectral diffusion) occurs within the inhomogeneous broadened transition. On deuteration the fluorescence lifetime of PTC increases and this should effect the Förster energy transfer process. Finally the guest isotope effect on the resonant phonon frequency is found to be negligible.

2. Experimental

The PTC in p-terphenyl crystals were grown from the Bridgeman furnace with guest concentrations, by initial weight ratio, of about 10^{-6} M. PTC-d_{14} was synthesized starting from perdeutero naphthalene according to a procedure developed in this laboratory [5].

The basic set-up for the photon-echo relaxation measurements is shown in fig. 1. An AVCO C-950 nitrogen laser was used to pump a modified AVCO dye-laser. This dye-laser system, with spectral bandwidth of ca. 4 cm^{-1} and pulse width of 5 ns, was used as exciting laser. The time-delay jitter of this system was found to be less than 500 ps. The probing pulse was obtained from a Molectron DL-200 dye-laser pumped by a Molectron UV-400 nitrogen laser. This system also has a pulse width of about 5 ns, but the spectral width is only 0.5 cm^{-1}. The time-delay jitter of this

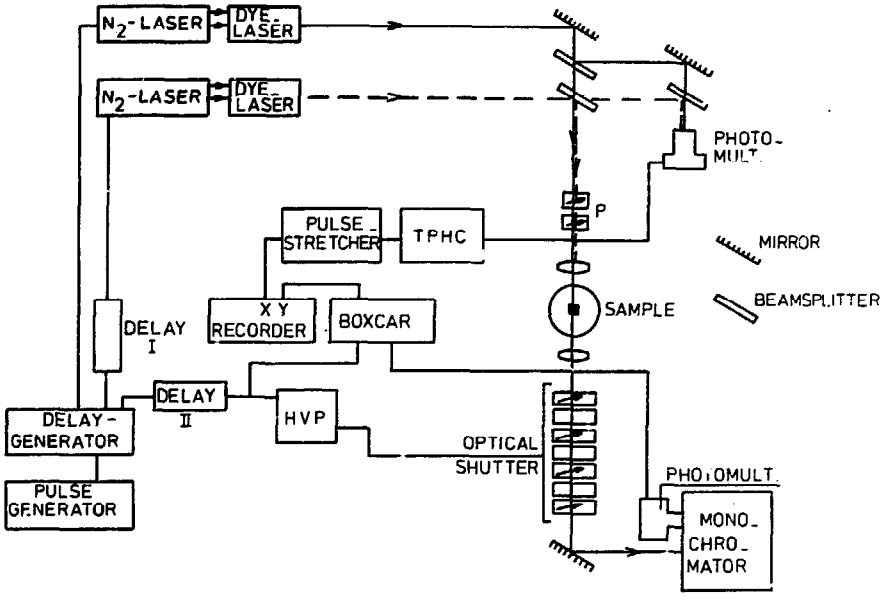

Fig. 1. Schematics of the photon-echo set-up with two separate nitrogen pumped dye-lasers. For details consult the experimental section.

system was found to be about 2 ns.

Both nitrogen lasers were independently triggered and the initial pulse separation was preset by introducing suitable trigger delays. The exact pulse separation is obtained from a calibrated time to pulse height converter (TPHC) which is triggered by the laser pulses, detected by a fast modified 1P28 photomultiplier [6]. The 2 μs output pulse of the TPHC is fed into a two-stage, fast sample and hold circuit.

The final dc output is either displayed on a voltmeter or fed into a channel of an $X-Y$ recorder. Digital delay generators were used, in the measurements reported here, to delay the probe pulse and shift the gate of the Pockells cell combination and the boxcar correspondingly. For further details of the photon-echo detection system we refer to ref. [3].

We have also performed echo relaxation measurements in a slightly different way, which is worth mentioning. In this set-up, the Molectron dye-laser system is internally triggered whereby part of the dye-laser output pulse is used to trigger the AVCO nitrogen laser. Due to the time-delay in output of the AVCO laser (ca. 500 ns) the pulse of the Molectron system must be delayed during this time. This is accomplished by passing this beam through an optical delay line [3]. Great care has to be taken in this set-up to prevent air-turbulence in the light path in the delay line, as otherwise the outcoming beam is spatially unstable. In this mode of operation the time-jitter between the exciting pulses was found to be less than 1 ns. We have performed experiments with both set-ups and the experiments reported here were mostly done with the latter set-up.

3. Results

3.1. Fluorescence lifetime

The fluorescence lifetimes of the $^1A_{1g} \leftarrow {}^1B_{2u}$ transition for PTC-h_{14} and -d_{14} were measured at 1.5 K in dilute and optically thin (ca. 5% absorption) p-terphenyl mixed crystals.

A Molectron dye-laser was used to excite an origin of the absorption system for perproto- at 16887 cm^{-1} [7] and for perdeutero-PTC at 16913 cm^{-1}. The upper state decay was then monitored on the screen of a transient digitizing system.

The higher energy sites were chosen for both the fluorescence and photon-echo decay experiments as in the perdeutero-PTC mixed crystal the lower energy site overlaps with other (not completely deuter-

ated) isotopes. For PTC-h_{14} we measured, in agreement with a recent report [8], a fluorescence lifetime of 23.5 ± 1 ns while for PTC-d_{14} a lifetime of 27.5 ± 1 ns was obtained. The isotope effect on the fluorescence lifetime of PTC is probably due to a reduction of the internal conversion rate on deuteration [9].

3.2. Photon-echo decay time

The photon-echo relaxation rates were measured also on dilute mixed crystals of PTC in *p*-terphenyl with 12% absorption for PTC-h_{14} and 9% absorption for PTC-d_{14}. Fig. 2 summarizes the results and the photon-echo intensity is shown to decay purely exponentially over the time-range of the measurements:

$$I(t) = I(0)\exp(-4t/T_2);$$

here t is the time interval between the exciting and probe-pulse and T_2 the transverse relaxation time in the optical analog of the Bloch equations [10].

From the slopes of the echo-decay curves we calculate for the dilute mixed crystals coherence lifetimes (T_2) of 45 ± 1 ns for PTC-h_{14} and 54 ± 1 ns for PTC-d_{14}. We note here that, within the error limits quoted, these T_2's are equal to $2T_1$ for both PTC isotopes. From the coherence lifetimes we then calculate *homogeneous* linewidths $(\pi T_2)^{-1}$ of 7.1 and 5.9 MHz for PTC-h_{14} and -d_{14} respectively at 1.5 K in these mixed crystals. Fig. 2 also shows that in a more concentrated crystal of PTC-h_{14} in *p*-terphenyl the echo-decay time is much faster. In this case we calculate an echo-decay time of 28 ± 1 ns. This number is in agreement with a previous report of T_2 for PTC-h_{14} [3] where actually the *same* crystal was used in the measurement of T_2.

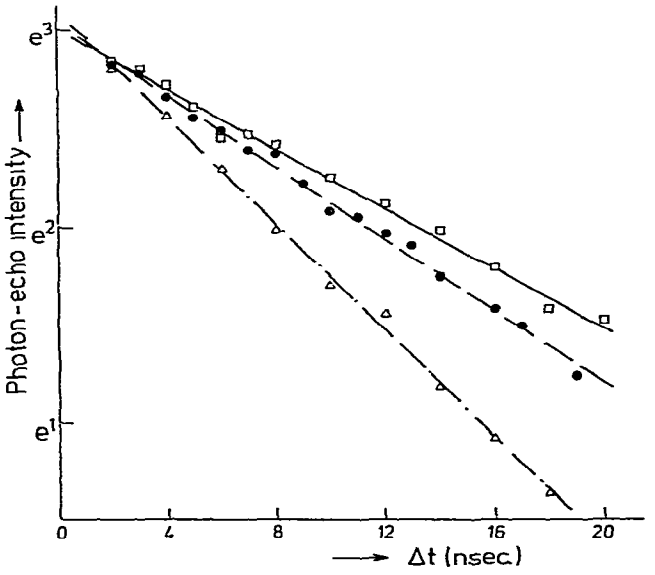

Fig. 2. Photon-echo intensity versus exciting pulse *increment* separation at 1.5 K. $\Delta t = 0$ corresponds to an initial 25 ns separation between the exciting pulses. All measurements refer to pentacene (PTC) in *p*-terphenyl-h_{14} mixed crystals. □ PTC d_{14} (ca. 2×10^{-8} M); • PTC-h_{14} (ca. 10^{-8} M); △ PTC-h_{14} (ca. 10^{-7} M).

We have also examined the effect of the exciting and probing laser intensity on the echo relaxation rate but found none, in agreement with the results of a similar study on ruby [11]. We thus conclude that the shortening of the echo-decay at higher concentrations is an intrinsic effect of the PTC in *p*-terphenyl mixed crystal.

4. Discussion

In a recent letter on optical phase relaxation of tetracene and pentacene in *p*-terphenyl [8] the following expression for the echo relaxation rate of pentacene was derived:

$$T_2^{-1} = 1/2T_{1f} + \sum_i (1/2\tau_i)\exp(-\Delta E_i/kT).$$

Here T_{1f} is the fluorescence lifetime of the excited state while ΔE_i and τ_i are the energy and lifetime respectively of the resonant phonons in either the ground and excited state. At very low temperature T_2 is therefore expected to converge to $2T_{1f}$ and this is indeed observed for both isotopes in the dilute mixed crystals. At slightly higher concentrations however the loss of coherence is increased over the emission rate and the conlcusion must be that energy transfer among the molecules is taking place. Recently Port et al. [12] showed that in dilute isotopically mixed crystals of naphthalene energy transfer among the monomers also occurs at guest concentrations higher than 10^{-3} M. A Förster [13] dipole–dipole energy transfer mechanism in this case was shown to be consistent with all results. The PTC transition we are concerned with, has a much larger transition-dipole and we therefore expect energy transfer to occur at much lower

guest concentrations than observed for naphthalene. An estimate of the PTC guest concentration can be made by assuming that the total integrated oscillator strength of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition in PTC is the same as for the corresponding transition in tetracene, namely 0.11 [14]. The origin of the PTC absorption spectrum certainly carries 40% of the total integrated intensity [15]. From this data and the optical density we calculate a PTC guest concentration of 10^{-7} M in the more concentrated mixed crystal, in which energy transfer is observed. We further calculate the rate of the spectral diffusion process in this 10^{-7} M crystal from the photon-echo decay time to be 2.7×10^7 s^{-1}. Incidentally we note here that this constant can now be identified with the constant $[T_2^*(0)]^{-1}$ of ref. [3]. At such a low guest concentration the rate of energy transfer thus is already comparable to the emission rate constant of 4×10^7 s^{-1}. We are presently engaged in a study of the concentration dependence of this excitation diffusion process. The energy transfer process itself, most likely, occurs between an excited and a ground-state pentacene molecule.

Without phonon-assistance it is essential then, in the Förster energy transfer mechanism, that the donor and acceptor (homogeneous) transitions overlap. We would therefore expect the effect of spectral diffusion on the echo relaxation time to be less pronounced in a perdeutero than in a perproto pentacene in *p*-terphenyl mixed crystal. Further experiments to ascertain the exact nature of the energy transfer process are mandatory as Förster energy transfer among excited states [16] presently cannot be ruled out.

Next to the isotope effect on the low-temperature photon-echo relaxation rate we have also examined the guest isotope effect on the resonant phonon-frequency (ΔE). From the temperature dependence of the photon-echo intensity of PTC-d_{14} in *p*-terphenyl at 16913 cm^{-1} we calculate ΔE to be 17 ± 2 cm^{-1}. As this is well within the error limit of the ΔE value of 18.7 ± 1 cm^{-1} of the corresponding site of PTC-h_{14} [3] we conclude that the guest isotope effect on the resonant phonon frequency is negligible.

5. Summary and conclusion

In this paper we have shown that in dilute mixed crystals of pentacene in *p*-terphenyl (ca. 10^{-8} M) at 1.5 K, the *homogeneous* linewidth, of the origin of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition, is only determined by the fluorescent decay of the upper state.

To the best of our knowledge this, in fact, is the first time that in a solid T_2 is found to be equal to $2T_1$. We anticipate that for *all* singlet–singlet transitions in *dilute* mixed crystals this is the case.

We have further shown that in slightly more concentrated crystals (ca. 10^{-7} M for PTC in *p*-terphenyl) T_2 considerably shortens and this is ascribed to spectral diffusion. The photon-echo thus seems an excellent probe to sense such effects.

We have also demonstrated that two separate nitrogen pumped dye-lasers can be advantageously used to study photon-echo relaxation. The effect of using a different spectral bandwidth for the exciting and probe-pulse however remains to be investigated and exploited.

Finally we note that it would be very interesting to compare the results of FID measurements [17,18] with those of photon-echo relaxation measurements on the *same* pentacene in *p*-terphenyl mixed crystals.

Acknowledgement

We are indebted to Berend Kwant for the synthesis of pentacene-d_{14}.

References

[1] N.A. Kurnit, I.D. Abella and S.R. Hartmann, Phys. Rev. 141 (1966) 391.
[2] N. Takeuchi and A. Szabo, Phys. Letters 50A (1974) 361.
[3] T.J. Aartsma and D.A. Wiersma, Chem. Phys. Letters 42 (1976) 520.
[4] C.K.N. Patel and R.E. Slusher, Phys. Rev. Letters 20 (1968) 1087.
[5] B. Kwant, J. Lab. Comp. (1977), to be published.
[6] G. Beck, Rev. Sci. Instr. 47 (1976) (537).
[7] J.H. Meyling and D.A. Wiersma, Chem. Phys. Letters 20 (1973) 383.
[8] T.J. Aartsma, J. Morsink and D.A. Wiersma, Chem. Phys. Letters 47 (1977) 425.
[9] B. Soep, A. Kellmann, M. Martin and L. Lindqvist, Chem. Phys. Letters 13 (1972) 241.
[10] F. Bloch, Phys. Rev. 70 (1946) 460.
[11] A. Compaan, L.Q. Lambert and I.D. Abella, Phys. Rev. Letters 20 (1968) 1089.

[12] H. Port, D. Vogel and H.C. Wolf, Chem. Phys. Letters 34 (1975) 23.
[13] T. Förster, Discussions Faraday Soc. 27 (1959) 7.
[14] A. Bree and L.E. Lyons, J. Chem. Soc. (1960) 5206.
[15] J.H. Meyling and D.A. Wiersma, unpublished results.
[16] R.M. Hochstrasser and A.C. Nelson, Opt. Commun. 18 (1976) 361.
[17] R.G. Brewer and A.Z. Genack, Phys. Rev. Letters 36 (1976) 959.
[18] A.Z. Genack, R. Macfarlane and R. Brewer, Phys. Rev. Letters 37 (1976) 1078.